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THE
THEORY
OF THE
PHOTOGRAPHIC
PROCESS
FOURTH EDITION

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CH. 10. MECHANISM OF SPECTRAL SENSITIZATION

often exceeds that of either of the dyes separately at the concentration in the emulsion. Hence, if the concentration of one dye is chosen for optimum spectral sensitization, the addition of a second often depresses spectral sensitivity.

Sometimes, however, the spectral sensitivity of a dye is increased on addition of a second substance. If the added material does not itself sensitize in the spectral region of the sensitizer, any increase in spectral sensitivity is clearly superadditive and the addendum may be said to supersensitize the sensitizer. If two dyes sensitize for the same spectral region, supersensitization is indicated if a mixture of the two yields materially ($0.1-0.3 \log E$ or greater) more sensitivity at any wavelength than a concentration of either showing the same absorption as the mixture, or if the spectral sensitivity at any wavelength achieved by the mixture is materially greater than that obtainable from any concentration of either dye alone.

Although many examples of supersensitization are known, only a small fraction of random combinations of dyes is effective in this way. Typically, supersensitization can occur at a small concentration ratio of the additional dye to sensitizer. The dye present in the smaller amount may then be regarded as the supersensitizer for the other as sensitizer. The supersensitizing effect, however, may be mutual, the spectral sensitization of each dye being increased by the presence of the other.²⁵ Typical supersensitizers are either dyes or colorless compounds showing strong absorption bands in the near-ultraviolet spectral region associated with electron systems similar to those of dyes. Some family regularities are recognized in supersensitization; for example, supersensitizable 2,2'-monomethinecyanines are likely to respond to styryl bases as supersensitizers²⁶ and other families of compounds have been recognized as supersensitizers for those dyes.²⁶

Supersensitizing dyes may sensitize in their own right but frequently not with conspicuous efficiency. No general relationship between the chemical structures of sensitizer and supersensitizer has emerged, although relations between their oxidation-reduction properties have been recognized.

The absorption maximum of the supersensitizer may be either at shorter or longer wavelengths than that of the sensitizer—no overlap of absorption bands or of the fluorescence band of the sensitizer with the absorption band of the supersensitizer is required. Sensitizers in the J state of aggregation tend to respond particularly well to supersensitizers, but strong supersensitization of H-aggregated dyes is observed, and the effect may occur, less strongly, with sensitizers showing the modified molecular absorption band on the grain surface. In the presence of supersensitizers, the J-band of the sensitizer may broaden

and is frequently but not always displaced to shorter wavelengths.^{2b,9s,25,27a-c} If the concentration of the supersensitizer is raised sufficiently relative to that of the sensitizer, the J-band of the sensitizer may disappear.^{27d} From the relative concentrations of the two dyes at which this happens, it has been estimated that the minimum size of the J-aggregate is three molecules.^{27d}

Supersensitization of J-aggregated sensitizers may be detected at a molar ratio of supersensitizer to sensitizer of $1:10^4$; maximum efficiency of supersensitization usually occurs in the range 1:20 to 1:1.

Supersensitization may be achieved by a variety of dye-supersensitizer interactions.^{28a} The supersensitizer may increase the spectral absorption of the sensitizer by inducing or intensifying a J-band. In some combinations these changes in absorption can be associated with a mutual increase in adsorption of both members to the grain surface, as when the sensitizer and supersensitizer are ions of opposite charge.^{28b} The characteristic absorption band of the supersensitizer sometimes disappears in the supersensitization of a J-aggregated sensitizer, and the mixture shows an absorption band for the dye system as a whole, broadened and bathochromically shifted from the position of the J aggregate of the sensitizer alone, sometimes analogous to the mixed aggregates in aqueous solution described by Scheibe^{29a} and Ecker.^{29b}

Desensitization of the intrinsic response by a supersensitized combination may be less than that of the sensitizer alone, sometimes an important contribution to the total increase in sensitivity. The most important effect of the supersensitizer is, however, to increase the efficiency of spectral sensitization as measured by the relative quantum yield. All these effects may operate simultaneously to produce the observed supersensitizing effect.

Figure 10.3 illustrates an example of supersensitization caused almost entirely by an increase in the efficiency of sensitization, that of 1,1'-diethyl-2,2'-cyanine by the styryl base 2-(p-diethylamino-styryl)benzothiazole.^{29c} The spectral absorptance at the J maximum of the sensitizer is little changed by the presence of the supersensitizer, but the relative quantum yield of sensitization is increased from about 0.06 to nearly 1.0. The efficiency of sensitization by J-aggregates alone is frequently low but can be raised by supersensitization, as in this example, although some J aggregating dyes whose excited levels are relatively high with respect to the conduction band of silver halide show high sensitizing efficiency without the necessity of being supersensitized.^{27c}

The most spectacular relative increases in spectral sensitivity are observed in the supersensitization of highly nonplanar dyes of the 2,2'-quinocyanine series,